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Electronic Structure and X-Ray Photoelectron Spectra of YNi_4B Compound

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The electronic structure of the ternary YNi_4B compound, crystallizing in the hexagonal CeCo_4B structure ($P6/mmm$ space group), was studied by X-ray photoelectron spectroscopy and *ab initio* calculations. Core levels and the valence band were investigated. The X-ray photoelectron spectroscopy valence band is compared with that obtained from *ab initio* calculations. The valence band spectrum at the Fermi level exhibits the domination of the $\text{Ni}(3d)$ states, which are hybridized with $4d$ states of Y and $2p$ states of B. The theoretical electronic specific heat coefficient γ derived from $N(E_F)$ is about $11.33 \text{ mJ}/(\text{mol K}^2)$ for experimental lattice parameters. The calculated bulk modulus is $B_0 = 1.61632 \text{ Mbar}$.

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1. Introduction

The RNi_4B compounds (R is a rare-earth metal) crystallize in the hexagonal CeCo_4B structure, which can be derived from RNi_5 by replacing two Ni atoms at the (2c) sites in every second layer by B atoms. In the CeCo_4B structure the Ni atoms occupy two kinds of crystallographic sites, (2c) and (6i), the rare-earth metal is also located in two sites, (1a) and (1b), and boron occupies one position (2d).

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We have also performed researches on the RNi_4B compounds employing both magnetic measurements and X-ray photoemission spectroscopy (XPS) [1–6]. CeNi_4B and PrNi_4B appeared to be paramagnetic, but the former showed evidence of mixed valence and Kondo effect [6] and the latter composition exhibited evidence of Pr_2Ni_7 impurity phase. The remaining RNi_4B compounds were ferromagnetic, with exceptionally large coercive field in the case of SmNi_4B ($H_c = 7$ T) [5].

For YNi_4B , Mazumdar et al. [7] observed paramagnetic behavior with an effective magnetic moment of about $0.2 \mu_B/\text{f.u.}$ However, below 12 K superconductivity can appear in this compound [7]; this is usually ascribed to an additional phase containing carbon. The secondary phase does not exceed 2%. Our measurements of the temperature dependence of the magnetic dc susceptibility give also evidence of superconductivity with $T_c^S \approx 12$ K [4] and the superconducting phase contribution is about 2%. It is confirmed by the presence of the diamagnetic response in the magnetization process measured at 4.2 K.

The electronic structure of YNi_4B was calculated some years ago by Ravindran et al. in [8]. These calculations were carried out using the tight binding linear muffin-tin orbital (TB-LMTO) method for local exchange-correlation potential of von Barth and Hedin. The eigenvalues were obtained with a set of 64 k points in the irreducible wedge of the first Brillouin zone of YNi_4B .

In this paper we present electronic and electrical resistivity studies of the YNi_4B compound.

2. Experimental details and method of calculation

The YNi_4B compound was prepared by the induction melting of stoichiometric amounts of the constituent elements in a water-cooled boat, under an argon atmosphere. The ingot was inverted and melted several times to insure homogeneity. The crystal structure was established by a powder X-ray diffraction technique, using $\text{Cu } K_\alpha$ radiation. The lattice constants are $a = 4.987 \text{ \AA}$ and $c = 6.948 \text{ \AA}$.

The XPS spectra were obtained with monochromatized $\text{Al } K_\alpha$ radiation with a photon energy of 1487.6 eV using a PHI 5700/660 Physical Electronics Spectrometer. The energy spectra of the electrons were analyzed by a hemispherical mirror analyzer with energy resolution of about ≈ 0.3 eV. The Fermi level, $E_F = 0$, was referred to the gold $4f_{7/2}$ binding energy at 84 eV. All emission spectra were measured immediately after breaking the sample in a vacuum of 10^{-10} Torr.

The electronic structure was calculated by the spin-polarized TB-LMTO method in the atomic sphere approximation (ASA) [9]. The self-consistent spin-polarized band calculations were performed for the experimental lattice parameters and also for the lattice parameters corresponding to the minimum of the total energy. The values of the atomic sphere radii were taken in such a way that the sum of all atomic sphere volumes was equal to the volume of the unit cell. In our case the unit cell contains two formula units ($N = 12$ atoms). The overlap volume of

the muffin-tin spheres is 8.7%. The Vosko–Wilk–Nusair local exchange-correlation [10] potential was used. The Perdew–Wang non-local exchange-correlation [11] was added. The scalar relativistic wave equation was solved. In the band calculations the initial atomic configurations were taken according to the periodic table of elements. We assume for Y: core(Kr) + $4d^15s^2$, for Ni: core(Ar) + $3d^84s^2$ and for B: core(He) + $2s^22p^1$. The computations were done for 750 k points in the irreducible wedge of the first Brillouin zone. The tetrahedron method [12] was used for integration over the Brillouin zone.

3. Results and discussion

XPS has become a widely used technique for studying the valence and core bands in transition metal compounds. The experimental photoemission spectrum of the valence band region of YNi₄B is shown in Fig. 1 (solid line). The most prominent peak is at 1.3 eV below E_F . The valence band spectrum exhibits the domination of Ni(3d) states at the Fermi level. The XPS valence spectrum is comparable with the results of our *ab initio* calculations of the electronic structure of YNi₄B. The computed photoemission spectrum (dashed line in Fig. 1) was obtained by weighting the density of states (DOS) with appropriate atomic cross-sections [13] for atomic photoemission and applying a convolution with a Lorentzian function, which accounts for the finite experimental resolution ($\sigma = 0.4$ eV).

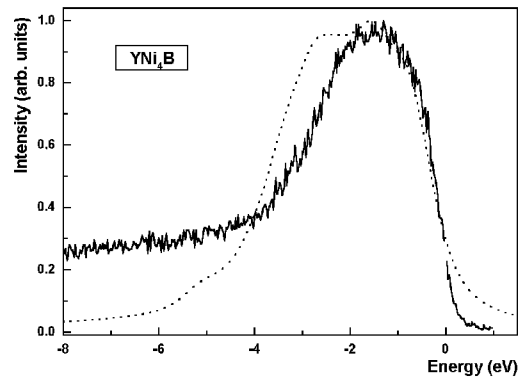


Fig. 1. Experimental (solid line) and theoretical (dashed line) valence band regions of YNi₄B.

The peaks of the XPS spectrum of YNi₄B at 870.3 eV and 853 eV were identified as Ni($2p_{1/2}$) and Ni($2p_{3/2}$) (see Fig. 2). The spin–orbit coupling value determined from XPS spectra of these $2p_{1/2}$ and $2p_{3/2}$ bands is equal to 17.3 eV. The positions of these peaks are similar to those observed in pure nickel. A core-level photoemission spectrum of Y(3d) is presented in Fig. 3. The doublet structure of

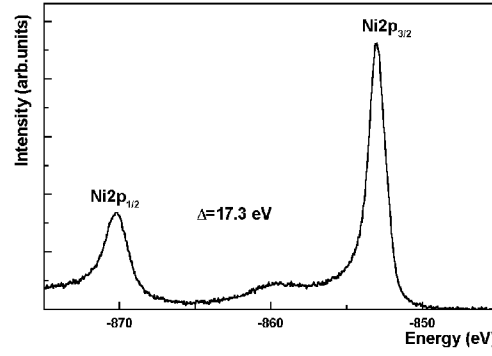


Fig. 2. $\text{Ni}(2p_{1/2})$ and $\text{Ni}(2p_{3/2})$ spectrum of YNi_4B .

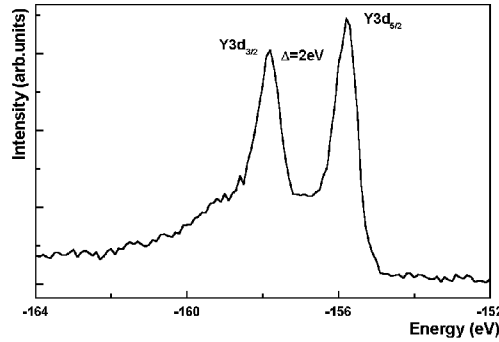


Fig. 3. $\text{Y}(3d)$ spectrum of YNi_4B .

the $\text{Y}(3d)$ state is visible. The positions of the peaks are in good agreement with metallic yttrium.

The ground state of YNi_4B is paramagnetic from electronic structure calculations. The total and local densities of states (DOS) for YNi_4B are displayed in Fig. 4a–e. The energy scale is presented in respect of the Fermi energy ($E_F = 0$). The common feature of the electronic structure of RNi_4B (where $\text{R} = \text{Ce}, \text{Gd}$) is the significant contribution of the d -states of Ni [1, 6]. For the most part of the total DOS for YNi_4B (Fig. 4) we also observed the contributions of the Ni atoms in (2c) and (6i) positions, which contain mainly d -states of nickel below the Fermi level. The different shapes of the partial DOS of Ni atoms in (2c) and (6i) positions (Fig. 4b,c) are caused by different types of atoms in the nearest neighborhood. The first peak in the total DOS (Fig. 4a) below the Fermi level (at -0.75 eV) is derived from d -states of Ni(2c) (Fig. 4b). The second peak of the total density of states (Fig. 4a) observed at -1.417 eV is a result of contributions of both d -states of Ni(2c) and Ni(6i) (Fig. 4b,c). The d -states of Y atoms give a small contribution (below 2 states/(eV cell)) from the whole region from -6 eV

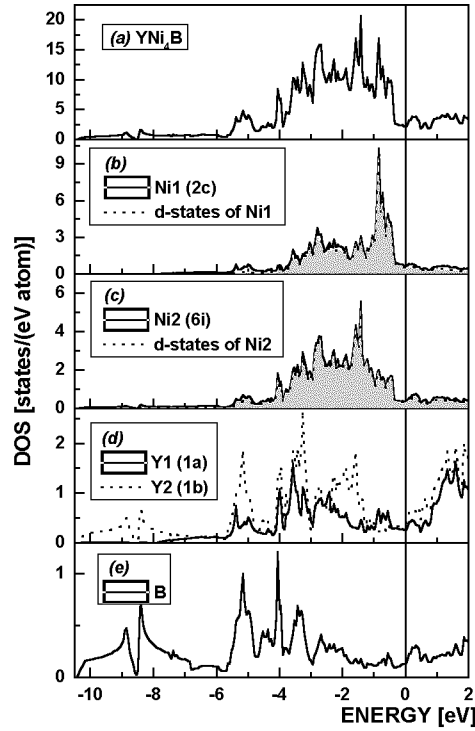
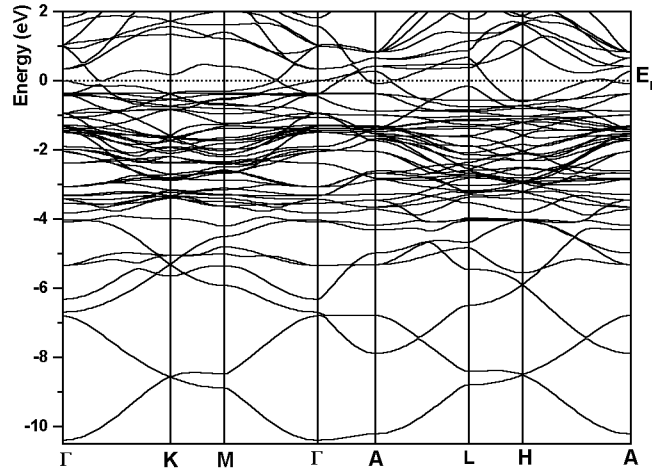
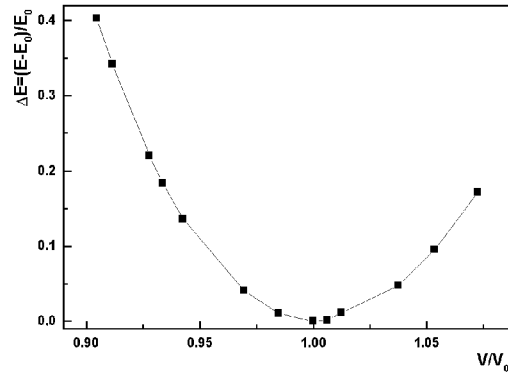


Fig. 4. The density of states of YNi_4B : (a) the total DOS in states/(eV f.u.); (b) the contribution of Ni1 atoms in (2c) site and d -states of Ni1 (dotted line, shaded); (c) the contribution of Ni2 atoms in (6i) site and d -states of Ni2 (dotted line, shaded); (d) the contribution of Y atoms in (1a) and (1b) sites; (e) the contribution of B atoms.

to the Fermi level (0 eV). The DOS contribution of boron atoms is visible below -7.5 eV. The band structure along various symmetry directions is demonstrated in Fig. 5. In the direction $K-M$ and H the bands do not cross the Fermi level. The bottom of the band structure (Fig. 5) has the parabolic shape (above -10.5 eV) arising just from s -states of B. The s -states of boron and s -states of nickel in (6i) site influence the shape of the lower part of the density of states (from -10.5 eV to -7.5 eV). The total and local DOS and the band structure of YNi_4B (Fig. 4a-e and Fig. 5) reveal the hybridization of d -states of Ni with d -states of Y and p -states of B.

The relative change of total energy as a function of unit cell volume of YNi_4B is presented in Fig. 6. The equilibrium volume and theoretical equilibrium lattice parameters are obtained from the minimum of total energy. The theoretical equilibrium lattice parameters are $a = 5.143$ Å and $c = 7.165$ Å. Thus, the theoretical values of lattice parameters are about 3.13% higher than the experimental ones. The density of states for YNi_4B is $N(E_F) = 4.249$ states/(eV cell) and

Fig. 5. The band structure of YNi₄B.Fig. 6. The relative change of total energy as a function of unit cell volume for YNi₄B.

4.785 states/(eV cell) for experimental lattice parameters and for lattice parameters from minimum of the total energy, respectively. The calculated electronic specific heat coefficient γ , derived from $N(E_F)$ using the relation

$$\gamma = \frac{\pi^2 k_B^2}{3} N(E_F) \quad (1)$$

(where k_B is the Boltzmann constant), is about 11.33 mJ/(mol K²) for the experimental lattice parameters a and c , and 12.75 mJ/(mol K²) for the lattice parameters from the minimum of total energy, respectively. These values of electronic specific heat coefficient are in good agreement with an earlier theoretical value of γ obtained from band calculations (12.96 mJ/(mol K²)) by Ravindran et al. [8]. The theoretically obtained values of γ are smaller than the experimentally observed for YNi₄B (14.1 mJ/(mol K²)) [14].

The total energy versus volume data were fitted to the six-term function, which was considered by Krasko and Olson in [15]:

$$E = E_1 + \frac{E_2}{V^{2/3}} + \frac{E_3}{V^{4/3}} + \frac{E_4}{V^{6/3}} + \frac{E_5}{V^{8/3}} + \frac{E_6}{V^{10/3}}. \quad (2)$$

Such a dependence of the total energy on atomic volume V is generated by the Murnaghan–Birch type equation of state [16, 17] to obtain the bulk modulus. The bulk modulus B is defined by the equations:

$$B = -V \frac{\partial p}{\partial V} = V \frac{\partial^2 E}{\partial V^2}, \quad (3)$$

where E is the total ground-state energy as a function of volume, p is the pressure, and B is evaluated at the minimum of energy E . The bulk modulus is $B_0 = 1.61632$ Mbar by our calculation.

The expression for the Debye temperature Θ_D , as suggested by Moruzzi et al. [18],

$$\Theta_D = 41.63 \left(\frac{r_0 B}{M} \right)^{1/2}, \quad (4)$$

where M is an atomic weight, r_0 is an atomic sphere radius, yields the value 272.89 K for YNi_4B .

4. Conclusions

The electronic structure calculations have shown that YNi_4B is paramagnetic. Below the Fermi level the total DOS contained mainly d -states of Ni atoms. The total, partial DOS and band structure of YNi_4B reveal the hybridization of d -states of Ni with d -states of Y and p -states of B. The theoretical electronic specific heat coefficient γ derived from $N(E_F)$ is about 11.33 mJ/(mol K²) for experimental lattice parameters. The obtained bulk modulus is $B_0 = 1.61632$ Mbar. The theoretical calculations of the valence band are in good agreement with the XPS spectrum. The valence band of the X-ray photoemission spectrum is composed mainly of the Ni(3d) band.

The calculated value of the Debye temperature ($\Theta_D = 273$ K) is in good agreement with experimental one ($\Theta_D = 240$ K) [19].

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